



Fabrication of visible-light active Fe_2O_3 -GQDs/NF- TiO_2 composite film with highly enhanced photoelectrocatalytic performance



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ABSTRACT

Visible-light active Fe_2O_3 -GQDs/NF- TiO_2 composite films were fabricated via sequential electro-deposition and electro-oxidation processes. The prepared photocatalytic films were extensively characterized using scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). The results revealed that graphene quantum dots (GQDs) and α - Fe_2O_3 particles were simultaneously deposited onto the surface of N and F co-doped TiO_2 (NF- TiO_2) simply using a graphite sheet instead of a Pt sheet as anode in the electro-deposition process. The NF- TiO_2 substrate obtained by calcining TiO_2 nanotubes (TiO_2 -NTs) in the presence of NH_4F displayed pyramid shapes with dominant (101) facets. Linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and Mott-Schottky (M-S) plots indicated that the generation, separation and transfer of photogenerated charges were greatly enhanced on the novel composite. The photocurrent density of Fe_2O_3 -GQDs/NF- TiO_2 was 4.2 times that on Fe_2O_3 / TiO_2 -NTs at 0.5 V vs. Ag/AgCl under visible light irradiation. For the photoelectrocatalytic (PEC) reduction of Cr(VI) using Fe_2O_3 -GQDs/NF- TiO_2 as photoanode with a Ti sheet as cathode, substantially enhanced activity was achieved due to the combined effect of visible-light-active components (α - Fe_2O_3 and NF- TiO_2) and excellent electron mediator (GQDs). The calculated reduction rate constant was 7 times that obtained on Fe_2O_3 / TiO_2 -NTs film. Furthermore, both the long-time photocurrent and cyclic PEC reduction of Cr(VI) indicated good stability of the composite film.

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1. Introduction

In recent decades, semiconductor photocatalysis has been recognized as one of the most promising methods for environmental remediation [1,2]. Based on photocatalysis, an improved performance was observed in the photoelectrocatalytic (PEC) process after the introduction of bias voltage, which promoted the separation of photogenerated electron–hole pairs [3–8]. In addition, the immobilized photocatalytic films in the PEC process can be easily reused, which is critical for future practical applications. However, it is still a great challenge to develop highly efficient photocatalytic material that can utilize more solar energy.

As the most extensively studied photocatalyst, pure TiO_2 can absorb only UV light and cannot be directly excited by visible light, which accounts for up to approximately 43% of solar radiation. Lattice doping and surface modification have both been investigated to overcome this problem and have proven effective [1,9–11]. Non-metal doping, such as N doping, is recognized as one of the most promising way to narrow the band gap and extend the response of TiO_2 into visible region [10,12]. However, the oxidative power of N-doped TiO_2 (N- TiO_2) under visible light is relatively low due to the formation of a mixed gap composed of N 2p and O 2p above the valence band (VB). For example, the degradation of formic acid, NH_3 or I^- barely proceeded on N- TiO_2 [13,14]. Previously, we observed the vital role of fluorine in tuning the band structure of N- TiO_2 [15]. Co-doping of F could enhance the oxidative power of N- TiO_2 and shift the conduction band (CB) to a more positive position [16,17].

Surface modification with another narrow band-based semiconductor is also a suitable option to improve the visible light activity of TiO_2 [18–20]. N-type hematite (α - Fe_2O_3 , 2.2 eV) is recognized as

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a promising candidate due to its high visible light absorption, rich abundance and low cost [21–23]. Enhanced photocatalytic activity under visible light has been reported when coupled with TiO_2 or N-TiO_2 [24–29]. Because the CB of $\alpha\text{-Fe}_2\text{O}_3$ lies below the CB of TiO_2 [27,28], only high-energy electrons of $\alpha\text{-Fe}_2\text{O}_3$, which constitute a small fraction of photogenerated electrons, can be transferred to the CB of TiO_2 [25,29]. Thus, raising the CB of $\alpha\text{-Fe}_2\text{O}_3$ or lowering the CB of TiO_2 may be beneficial for the electron transfer process. Because the co-doping of N and F can lower the CB position of TiO_2 [15], the construction of a $\alpha\text{-Fe}_2\text{O}_3/\text{NF-TiO}_2$ composite should be a more suitable choice than $\alpha\text{-Fe}_2\text{O}_3/\text{N-TiO}_2$ or $\alpha\text{-Fe}_2\text{O}_3/\text{TiO}_2$. Low-energy electrons on $\alpha\text{-Fe}_2\text{O}_3$ can be more efficiently utilized in this composite.

Moreover, carbon materials have shown excellent promoting effect in the electron transfer process [30–34]. For example, carbon nanotube, carbon quantum dots, graphene and graphene quantum dots (GQDs) were all members of carbon family [35–38]. Recently, graphene quantum dots (GQDs) with a small size (<20 nm) have drawn considerable attention. GQDs are intriguing in terms of their ability to accept and transfer photogenerated electrons due to pronounced quantum confinement and edge effects. Thus, the performance of $\alpha\text{-Fe}_2\text{O}_3/\text{NF-TiO}_2$ can be further enhanced after the proper introduction of GQDs.

Herein, we report the first study and fabrication of a $\text{Fe}_2\text{O}_3\text{-GQDs/NF-TiO}_2$ composite film with the aim of achieving highly efficient electron generation, separation and transfer. The NF-TiO_2 substrate with pyramid-shape and dominant (101) facets was first prepared by calcining TiO_2 nanotubes ($\text{TiO}_2\text{-NTs}$) with the assistance of NH_4F . The most stable (101) facets was reported to be more reductive than the star facets of (001) [39–41], where photo-deposition of Pt and reduction of O_2 preferentially occurred [40,42]. Herein, (101) facets acted as highly active electron reservoirs. $\alpha\text{-Fe}_2\text{O}_3$ and GQDs were deposited onto the surface of NF-TiO_2 via sequential electro-deposition and electro-oxidation processes (Scheme 1). GQDs can be simultaneously deposited onto the surface of $\alpha\text{-Fe}_2\text{O}_3/\text{NF-TiO}_2$ simply using a graphite sheet instead of a Pt sheet as anode in the electro-deposition process. The generation, separation and transfer of photogenerated charges on the prepared film electrodes were compared using linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and Mott-Schottky (M-S) plots. Moreover, Cr(VI) , a carcinogen and mutagen was used as a model pollutant for capturing the cathode electrons, with coexisting organic pollutants as hole scavengers. Due to the combined effect of visible-light-active components ($\alpha\text{-Fe}_2\text{O}_3$ and NF-TiO_2) and the excellent electron conductors (GQDs), a highly enhanced PEC performance was demonstrated using $\text{Fe}_2\text{O}_3\text{-GQDs/NF-TiO}_2$ as photoanode and a Ti sheet as cathode.

2. Experimental

2.1. Preparation of the $\text{Fe}_2\text{O}_3\text{-GQDs/NF-TiO}_2$ film electrode

NF-TiO_2 film was obtained by calcining amorphous $\text{TiO}_2\text{-NTs}$ film (prepared by a traditional anodizing process [27,43]) in the presence of NH_4F at 450°C for 2 h (Scheme 1). $\text{TiO}_2\text{-NTs}$ can be simultaneously etched and doped by HF and NH_3 originating from NH_4F decomposition. As a control experiment, N-TiO_2 was also prepared using NH_4Cl instead of NH_4F in the calcination process. The initial ratio of NH_4F to Ti substrate (cm^2) was maintained at an optimal value of 0.2 g/cm^2 .

$\text{Fe}_2\text{O}_3\text{-GQDs/NF-TiO}_2$ films were prepared via consecutive electro-deposition and electro-oxidation processes (Scheme 1). $\text{Fe}_2\text{O}_3/\text{NF-TiO}_2$ was also prepared for comparison. The two different films were fabricated using different anodes (Pt sheet or graphite) in the electro-deposition process. For the deposition of

Fe_2O_3 , Fe^{3+} was first adsorbed onto the surface of NF-TiO_2 by soaking the NF-TiO_2 film in $\text{Fe}(\text{NO}_3)_3$ aqueous solution (0.1 M) and then converted to Fe^0 in the electro-deposition process. Finally, the electro-deposited Fe^0 was transformed to Fe_2O_3 via anodization in a 1.0 M KOH aqueous solution for 2 min. As controls, $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$ and $\text{Fe}_2\text{O}_3/\text{N-TiO}_2$ were also prepared in a manner similar to the $\text{Fe}_2\text{O}_3/\text{NF-TiO}_2$ preparation process except that TiO_2NTs or N-TiO_2 was used as the substrate for Fe_2O_3 loading instead of NF-TiO_2 .

2.2. Characterization

The morphology and structure of the prepared film samples were observed by a scanning electron microscope (SEM, Hitachi S-4800, Tokyo, Japan) and a high-resolution transmission electron microscope (HRTEM, JEOL JEM-2010, Tokyo, Japan). The chemical state of component elements in the film samples was investigated by a VG Thermo Escalab 220i-XL X-ray photoelectron spectroscopy (XPS) with Al $K\alpha$ at 1,486.6 eV. The binding energies of Ti 2p, O 1s, C 1s, Fe 2p, N 1s and F 1s were referenced against C 1s (284.6 eV). The crystal phases were detected by X-ray diffractometry (XRD) using a Bruke Regaku D/Max-2500. The vibration modes were detected by Raman spectra which were recorded on a thermo scientific DXR with exciting wavelength of 633 nm. The diffuse reflectance UV–vis absorption was recorded on a Hitachi U-3010 spectrophotometer. The photo-response of the prepared films was tested under chopped light irradiation (500 W Xe lamp, Shanghai lancheng) by an electrochemical station (CHI 660E). EIS analysis and M-S plots were also measured in a three-electrode configuration by a CHI 660E electrochemical station.

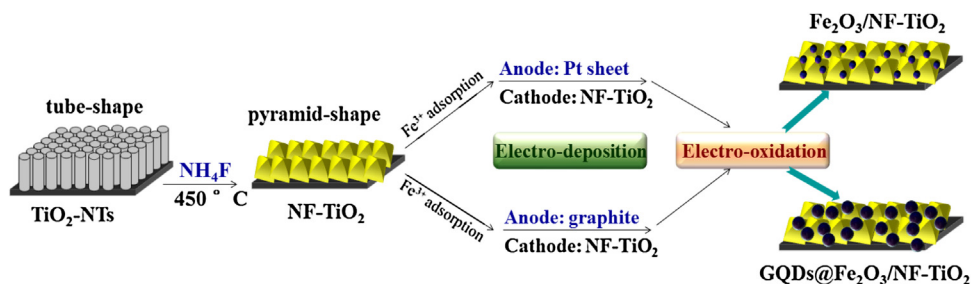
2.3. PEC study

Unless otherwise noted, the PEC activities of the prepared film electrodes (anode) were compared via the PEC reduction of Cr(VI) (80 μM) with Na_2SO_4 (0.2 mol/L) as the electrolyte and 1 mM EDTA as a hole scavenger. A constant DC potential of 2.0 V was applied to the photoanode with a Ti sheet as the cathode. The photoanode was irradiated by visible light ($\lambda > 420\text{ nm}$, ca. 80 mW cm^{-2}) emitted from a halogen lamp (CEL-IW500, Beijing Teach Jinyuan Technology Co., Ltd.) fitted with a cut-off filter and surrounded by a cooling water jacket. Before turning on the light, the electrode was immersed in Cr(VI) solution for 30 min to achieve adsorption-desorption equilibrium. Typically, the initial solution pH was adjusted to 3.0. The concentration of Cr(VI) at different time intervals was measured using the 1,5-diphenylcarbazide colorimetric method [44,45] on a UV–vis spectrophotometer (UV-2102PC, Unico Instruments Co., Ltd.). The purple complex of Cr(VI) 540 nm after adding chromogenic agent was barely affected by coexisting EDTA (Fig. S1). Meanwhile, pH variations as a function of PEC reaction time were also monitored (Fig. S2). In addition, the concentrations of coexisting organics, including EDTA (1.0 mM), phenol (10 mg/L), and methylene blue (MB, 10 μM) during the PEC process were also monitored. The colorless phenol and EDTA were detected by HPLC, whereas the MB dye was monitored by its maximum absorption at 664 nm on a UV–vis spectrophotometer.

3. Results and discussion

3.1. SEM and HRTEM

The prepared film electrodes were first characterized by SEM to investigate possible morphology changes. As shown in Fig. 1a, the $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$ surface was composed of TiO_2 nanotubes and Fe_2O_3 particles. Pyramid-shaped NF-TiO_2 was observed after calcining the $\text{TiO}_2\text{-NTs}$ substrate in the presence of NH_4F (Fig. 1b).



Scheme 1. Schematic depicting the preparation of Fe₂O₃/NF-TiO₂ and Fe₂O₃-GQDs/NF-TiO₂ films.

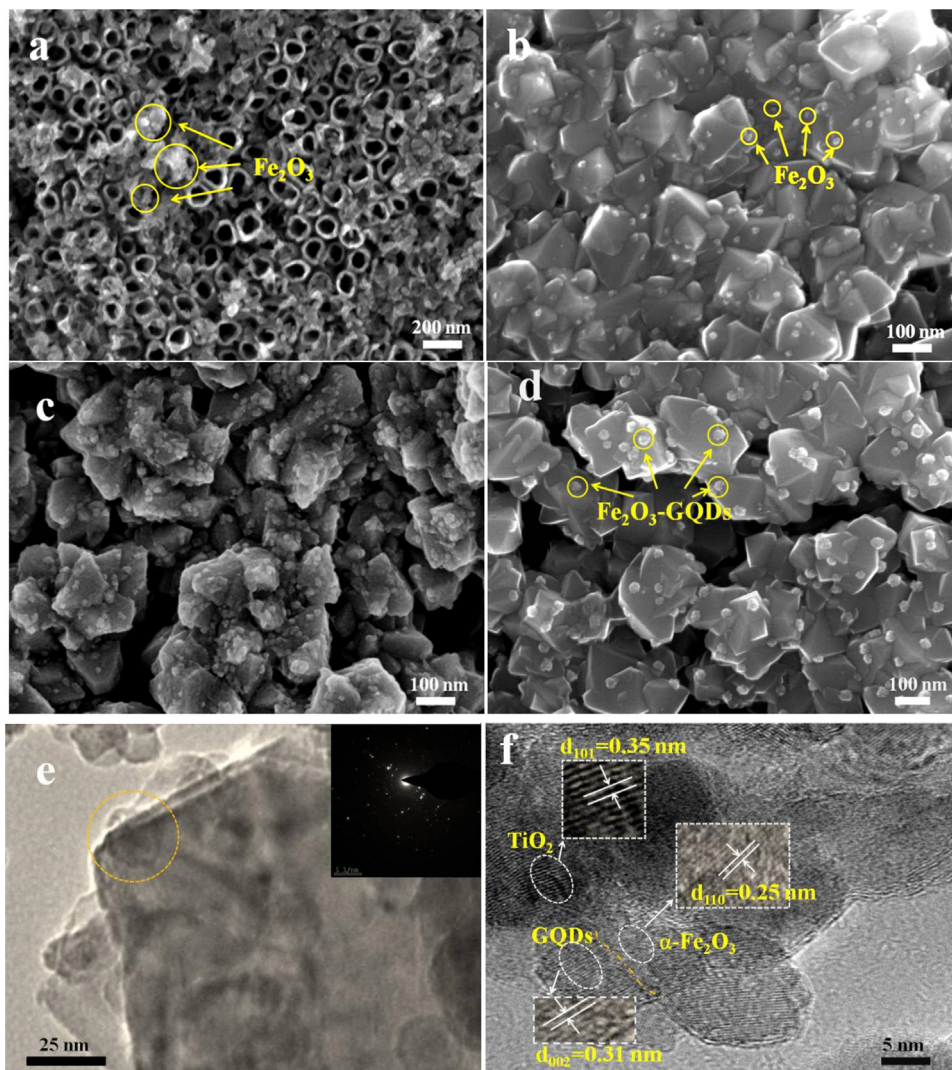


Fig. 1. SEM images of (a) Fe₂O₃/TiO₂-NTs, (b) Fe₂O₃/NF-TiO₂, (c) Fe₂O₃-GQDs/NF-TiO₂ (intermediate state) and (d) Fe₂O₃-GQDs/NF-TiO₂; (e) TEM and (f) HRTEM images of Fe₂O₃-GQDs/NF-TiO₂.

A control experiment using pure Ti foil instead of TiO₂-NTs was also performed to understand this interesting phenomenon. No pyramid-shaped structures were observed under identical calcination conditions (Fig. S3a). Moreover, a TiO₂-NTs surface was also calcined in the presence of NH₄Cl. The use of NH₄Cl instead of NH₄F led to the formation of particle-shaped products (Fig. S3b). In brief, the use of tubular structures as precursors and NH₄F as the additive were both essential for the formation of pyramid-shaped NF-TiO₂.

For Fe₂O₃/NF-TiO₂, smaller Fe₂O₃ particles (10–15 nm) were more uniformly deposited and dispersed on the surface of NF-TiO₂

(Fig. 1b). Interestingly, using different anodes (Pt sheet or a graphite sheet) during the electro-deposition process will lead to the formation of different Fe₂O₃-loaded electrodes (Fe₂O₃/NF-TiO₂ and Fe₂O₃-GQDs/NF-TiO₂). For example, as shown in Scheme 1, when a graphite sheet is used as the anode for the electro-deposition of Fe nanoparticles, graphite will be exfoliated simultaneously (Fig. S4) and will cover the surface of NF-TiO₂. As shown in Fig. 1c, the intermediate state was captured when the next oxidation step was not performed. The surface of NF-TiO₂ and deposited Fe⁰ nanoparticles was clearly covered by graphite-originated material. When

this intermediate state was further electrochemically oxidized in 1.0 mol/L KOH aqueous solution, Fe^0 was converted to Fe_2O_3 and the graphite-originated cover disappeared, leaving a clean NF-TiO₂ surface. However, the particle size loaded onto NF-TiO₂ (Fig. 1d) was observed to be considerably larger than that on $\text{Fe}_2\text{O}_3/\text{NF-TiO}_2$ using Pt as anode in the electro-deposition process. High-resolution TEM (HRTEM) was performed to obtain more detailed structural information. Fig. 1e illustrates that particles with a diameter of approximately 18 nm were loaded on the pyramid-shaped substrate. The HRTEM image of the selected area is presented in Fig. 1f. After fast Fourier transform (FFT), the lattice fringes of TiO₂, $\alpha\text{-Fe}_2\text{O}_3$ and GQDs can all be identified. For example, the lattice fringe spacing of 0.31 nm corresponds to the lattice fringes of (002) planes of GQDs [46,47], whereas the values of 0.25 and 0.35 nm were ascribed to the (110) plane of $\alpha\text{-Fe}_2\text{O}_3$ [48] and the (101) plane of anatase TiO₂, respectively.

3.2. XRD and raman spectra

XRD patterns of the prepared film electrodes were investigated, and the results are shown in Fig. 2A. The diffraction peaks at 25.3°, 37.9°, 48.1°, 54.0°, 55.1°, 68.8°, 70.3° and 75.1° correspond to (101), (004), (200), (105), (211), (116), (220) and (215) planes of anatase TiO₂, respectively. Distinct Rutile (110) signal can be observed in NF-TiO₂ (curve a). The presence of a small fraction of rutile may be beneficial for electron-hole separation under irradiation due to the formation of heterojunction. As for $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$ (curve b), pure anatase TiO₂ and distinct signals of the Ti substrate were observed. The characteristic diffraction peaks corresponding to $\alpha\text{-Fe}_2\text{O}_3$ (JCPDS No. 33-0664) can also be observed [22]. However, very weak $\alpha\text{-Fe}_2\text{O}_3$ signals can be observed in either $\text{Fe}_2\text{O}_3/\text{NF-TiO}_2$ or $\text{Fe}_2\text{O}_3\text{-GQDs}/\text{NF-TiO}_2$, which is probably due to the relatively small amount. Furthermore, Raman spectrum was carried out to confirm the presence of Fe_2O_3 . As shown in Fig. 2B, typical A_{1g} and E_{1g} Raman modes of $\alpha\text{-Fe}_2\text{O}_3$ [26] can be observed in both $\text{Fe}_2\text{O}_3/\text{NF-TiO}_2$ and $\text{Fe}_2\text{O}_3\text{-GQDs}/\text{NF-TiO}_2$.

Compared to $\text{Fe}_2\text{O}_3/\text{NF-TiO}_2$, a weak signal at 26.4° can be observed on $\text{Fe}_2\text{O}_3\text{-GQDs}/\text{NF-TiO}_2$ (Fig. S5), which is different from the characteristic and sharp diffraction peaks of either raw graphite (26.5°) [49] or expanded graphite (26.6°) [50]. Recently, Parvez et al. reported the electrochemical exfoliation of graphite into a graphene sheet, where the exfoliated products displayed a characteristic XRD peak at 26.3° [51]. The electrodeposition process (Scheme 1) in the present study is highly similar to Parvez's procedure, where graphite and Na_2SO_4 (which exhibited a pronounced exfoliation efficiency) were used as the anode and electrolyte, respectively. In addition to electro-deposition, subsequent electro-oxidation was added in the present study, which may destroy the sheet structure of graphene, leading to the small particle-shaped GQDs. The sp² configuration of GQDs was further verified by Raman spectrum. As shown in Fig. 2B, distinct peaks of the D band (1345 cm⁻¹) and G band (1603 cm⁻¹) of graphene [52] can be observed on $\text{Fe}_2\text{O}_3\text{-GQDs}/\text{NF-TiO}_2$, whereas no such peaks appeared on $\text{Fe}_2\text{O}_3/\text{NF-TiO}_2$. These results illustrate that GQDs were simultaneously formed and deposited together with Fe_2O_3 onto the surface of NF-TiO₂.

3.3. XPS

The chemical composition of $\text{Fe}_2\text{O}_3\text{-GQDs}/\text{NF-TiO}_2$ was further revealed by XPS spectra. As shown in Fig. 3A, signals of Ti 2p, O 1s, C 1s, Fe 2p, N 1s and F 1s can be observed. The N 1s and F 1s spectra, displayed in the insert of Fig. 3A, indicated the presence of O-Ti-N [53] and Ti-F species [54]. The high-resolution spectrum of C 1s (Fig. 3B) revealed the presence of C=C (284.4 eV), C-C (284.8 eV), C-O (285.4 eV) and O-C=O (288.2 eV) species [55]. As for Fe 2p

(Fig. 3C), the two peaks at 711.2 eV and 724.8 eV were ascribed to Fe 2p_{1/2} and Fe 2p_{3/2}, respectively. The distance between Fe 2p_{1/2} and Fe 2p_{3/2} is 13.6 eV, corresponding to Fe³⁺ in $\alpha\text{-Fe}_2\text{O}_3$ [56,57]. An approximately 0.8 eV positive shift in the binding energy of Fe 2p can be observed in $\text{Fe}_2\text{O}_3\text{-GQDs}/\text{NF-TiO}_2$ relative to that in $\text{Fe}_2\text{O}_3/\text{NF-TiO}_2$. However, a negligible shift was observed for Ti 2p (Fig. 3D). Therefore, the presence of GQDs appears to play a vital role in affecting the electronic environment around the Fe atoms. Because it has been verified by HRTEM (Fig. 1d) that the GQDs and Fe_2O_3 nanoparticles were in contact with each other, the sp² configuration of C=C bonds in GQDs will aid in the dispersion of electron density from Fe atoms to GQDs. Thus, the electron density around Fe_2O_3 will decrease, resulting in a higher binding energy [58]. In summary, it is reasonable to speculate that the electronic state of Fe_2O_3 is considerably different due to being covered by GQDs, which leads to the formation of $\text{Fe}_2\text{O}_3\text{-GQDs}$ loaded onto pyramid-shaped NF-TiO₂.

3.4. Electrochemical characterizations

The photocurrent response of the prepared films was tested and compared in 0.1 M Na_2SO_4 and Na_2SO_3 mixed aqueous solution under both chopped visible light ($\lambda > 420$ nm) and UV-vis light irradiation. As illustrated in Fig. 4, the $\text{Fe}_2\text{O}_3\text{-GQDs}/\text{NF-TiO}_2$ film exhibited the highest current density. Interestingly, large dark currents were always observed on NF-TiO₂ based samples. For more accurate comparison of the photocurrent density among different photoanodes, the dark currents were deducted and the results were shown in Fig. S6. Under visible light irradiation (Fig. S6A), the photocurrent density was -0.252 mA/cm^2 at 0.5 V vs. Ag/AgCl on $\text{Fe}_2\text{O}_3\text{-GQDs}/\text{NF-TiO}_2$, which was approximately 4.2 times that of $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$ (-0.059 mA/cm^2). Compared to pristine TiO₂-NTs, which cannot be excited by visible light, a greatly enhanced current density was also observed on $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-NTs}$ (Fig. S7), indicating that Fe_2O_3 acts as a visible light sensitizer. In addition, although the $\text{Fe}_2\text{O}_3/\text{NF-TiO}_2$ film (Fig. 4A, curve c) was prepared by a similar process as the $\text{Fe}_2\text{O}_3\text{-GQDs}/\text{NF-TiO}_2$ film, a greatly enhanced photocurrent response was observed on the latter one. The difference was ascribed to the introduction of GQDs, which may be beneficial for electron transfer. Moreover, the onset potential of different photoanodes were also compared (Fig. S8) [59,60]. It showed that more negative onset potential and increased photocurrent density can be observed on $\text{Fe}_2\text{O}_3\text{-GQDs}/\text{NF-TiO}_2$ film electrode.

EIS measurements were performed as EIS Nyquist plots can provide useful information on the electron-transfer process across the electrode-electrolyte interface. The EIS Nyquist plots of the different film electrodes were compared and the results were presented in Fig. S9. It can be observed that $\text{Fe}_2\text{O}_3\text{-GQDs}/\text{NF-TiO}_2$ exhibited smallest circular radius both in the dark and under visible light irradiation. Since small circular radius typically indicates a lower charge transfer resistance [61], lowest charge transfer resistance can be deduced on $\text{Fe}_2\text{O}_3\text{-GQDs}/\text{NF-TiO}_2$. In order to clarify the role of GQDs, The EIS Nyquist plots of $\text{Fe}_2\text{O}_3/\text{NF-TiO}_2$ and $\text{Fe}_2\text{O}_3\text{-GQDs}/\text{NF-TiO}_2$ were also compared. As shown in Fig. 5A, the introduction of GQDs can greatly reduce charge transfer resistance.

In addition to EIS analysis, M-S plots under dark conditions were also investigated to compare the charge carrier density of different film electrodes. The carrier density can be deduced from the slopes of the M-S plots using the following equation [62]:

$$C_{SC}^{-2} = \frac{2}{\epsilon_0 \epsilon N_D} (E - E_{fb} - \frac{kT}{e}) \quad (1)$$

where C_{SC} is the space-charge layer capacitance, N_D is the dopant density, ϵ_0 is the vacuum permittivity, ϵ is the relative dielectric constant of the oxide film, k is the Boltzmann constant, T is the

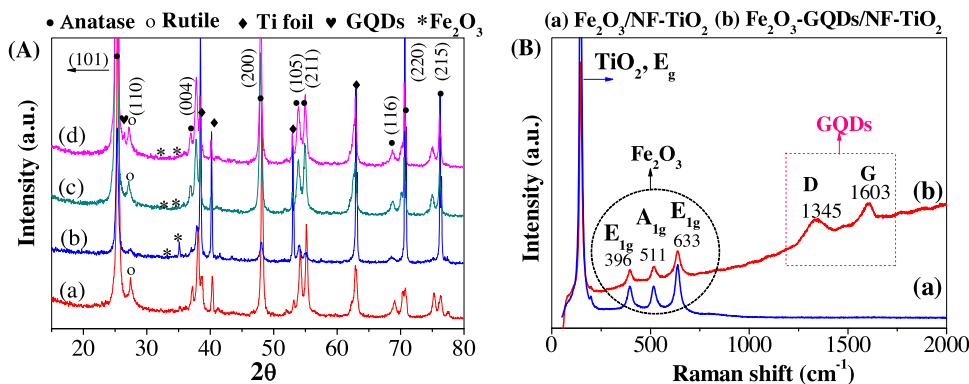


Fig. 2. (A) XRD patterns of NF-TiO₂ (a), Fe₂O₃/TiO₂-NTs (b), Fe₂O₃/NF-TiO₂ (c) and Fe₂O₃-GQDs/NF-TiO₂ (d); (B) Raman spectra of Fe₂O₃/NF-TiO₂ (a) and Fe₂O₃-GQDs/NF-TiO₂ (b).

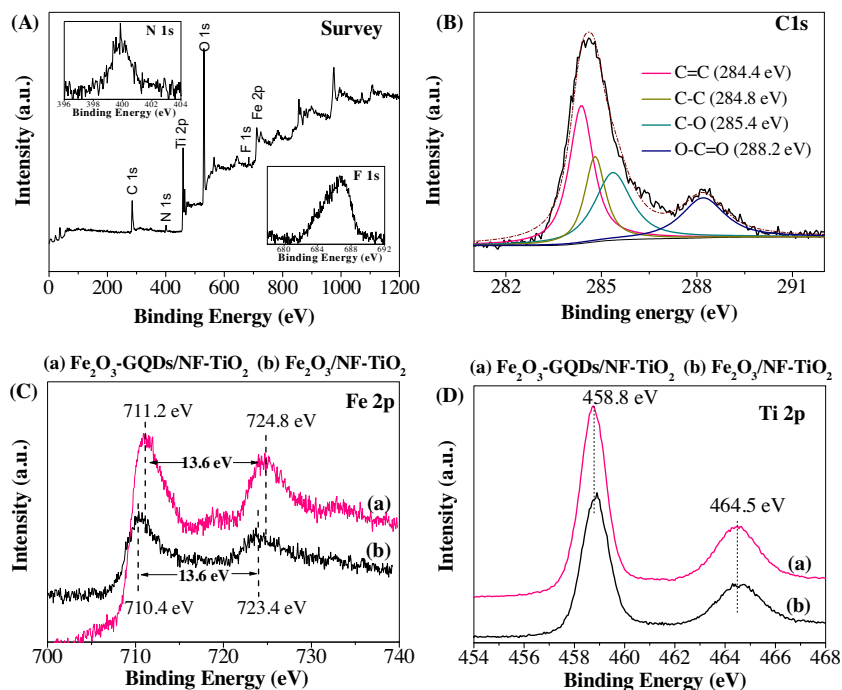


Fig. 3. (A) XPS survey spectrum taken from the surface of Fe₂O₃-GQDs/NF-TiO₂, insert: XPS spectra of N 1s and F 1s; (B) High-resolution XPS spectra of C 1s region; (C) Fe 2p and (D) Ti 2p region for Fe₂O₃-GQDs/NF-TiO₂ and Fe₂O₃/NF-TiO₂.

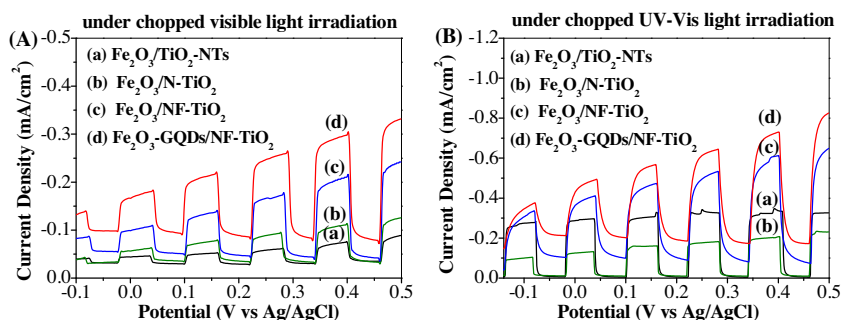


Fig. 4. Photocurrent response of different films under the irradiation of (A) chopped visible light (λ > 420 nm) and (B) chopped UV-vis light.

temperature and kT/e is a negligibly small correction term. As illustrated in Fig. 5B, the slope observed on Fe₂O₃-GQDs/NF-TiO₂ was much smaller after the introducing of GQDs, indicating higher carrier density. Thus, Fe₂O₃-GQDs/NF-TiO₂ is highly likely to achieve a better PEC performance when it is used for the removal of pol-

lutants due to the easier generation and transfer of electron-hole pairs.

Overall, easier generation, more efficient separation and enhanced transfer efficiency of photogenerated electron-hole pairs can be achieved on an Fe₂O₃-GQDs/NF-TiO₂ due to the combined

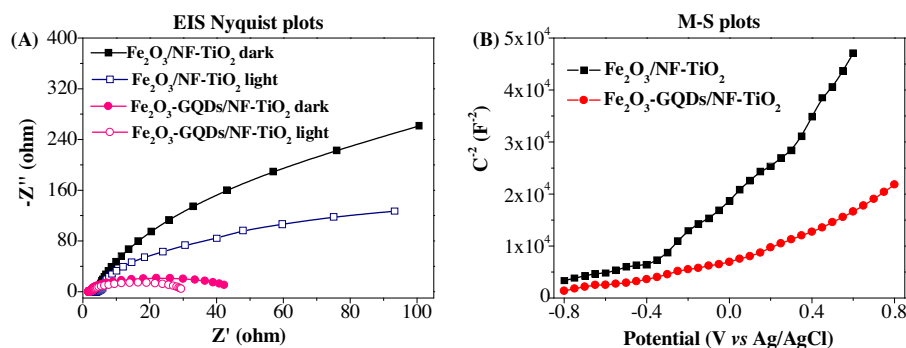


Fig. 5. (A) EIS Nyquist plots measured in 0.5 M Na₂SO₄ aqueous solution with a frequency range of 100 kHz–0.01 Hz and a scan rate of 5 mV s⁻¹; (B) M-S plots of different film electrodes measured in 0.2 M Na₂SO₄ at 500 Hz.

effect of the visible-light-active components (Fe₂O₃ and NF-TiO₂) and the excellent electron mediator (GQDs). Therefore, the utilization of the superior photoelectrochemical properties for PEC applications in environmental remediation should be further investigated.

3.5. PEC activity

Hexavalent chromium (Cr(VI)) is toxic, carcinogenic and highly mobile in water and soil. Every year, a tremendous amount of wastewater containing Cr(VI) is discharged from industrial processes, such as electroplating, leather tanning, wood preservation and pigment use [15,44]. Thus, the detoxification of Cr(VI) is of vital importance. Cr(VI) is typically reduced to nontoxic Cr(III), which can be removed from aqueous solutions in the form of Cr(OH)₃. Compared to traditional processes for Cr(VI) reduction, photocatalytic and PEC methods are efficient and environmentally friendly, which can avoid secondary pollution [63].

In the present study, Cr(VI) was selected as a model pollutant. The prepared film samples were tested as photoanode with a Ti sheet as cathode for the reduction of Cr(VI) under visible light. As shown in Fig. 6A, Fe₂O₃-GQDs/NF-TiO₂ exhibited the highest PEC activity among the tested photoanodes. The estimated rate constant (k : 0.0231 min⁻¹) (Fig. 6B) was 7 times that of Fe₂O₃/TiO₂-NTs (k : 0.0033 min⁻¹). Since GQDs were reported to enhance the PEC activity of TiO₂ [35,36], control experiment using GQDs/NF-TiO₂ as photoanode was also carried out in the present study. As shown in Fig. 6B, about 4 times rate constant enhancement can still be observed on Fe₂O₃-GQDs/NF-TiO₂ relative to GQDs/NF-TiO₂ (k : 0.0062 min⁻¹). Thus, the co-loading of Fe₂O₃ and GQDs are very important. Besides, pH of the solutions before, during and after photocatalytic reaction were also measured and the results were presented in Fig. S2. It can be observed that pH of the solutions gradually increased from 3.0 to 3.5.

The optimal Fe₂O₃-GQDs/NF-TiO₂ film was further tested in single photocatalytic (PC) or electrocatalytic (EC) processes to confirm the superiority of the PEC process. As shown in Figs. 6C–D, a synergistic effect can be observed in the PEC process, and the synergistic factor (SF) was calculated to be 2.9 according to the following equation [64]:

$$SF = \frac{k_{PEC}}{k_{PEC} + k_{EC}} \quad (2)$$

where k_{PEC} , k_{PC} and k_{EC} represent rate constants for Cr(VI) reduction in the PEC, PC and EC processes, respectively.

Because the photocatalytic performance of Fe₂O₃-GQDs/NF-TiO₂ can be markedly increased with the assistance of applied potential, the effect of different applied potentials was investigated, and the results are presented in Fig. 7. The PEC reduction of Cr(VI) was easier at a higher applied potential within the range

of 1.0 V–3.0 V. Moreover, the efficiency of electrochemical enhancement (E , in%) was estimated.

$$E = \left(\frac{k_{PEC} - k_{PC}}{k_{PEC}} \right) \times 100\% \quad (3)$$

According to the above equation [65], the E value at 1.0 V was calculated to be 45.6%, whereas it increases considerably to 87.0% at 2.0 V. However, the enhancement trend slowed down, with an E value of 93.6%, when the applied potential further increased to 3.0 V. Thus, 2.0 V was selected for the following study for the purpose of energy conservation.

A large amount of organic pollutants are also observed in Cr(VI)-containing wastewater. For example, EDTA has been detected as a common chelating agent, which may arise from various industrial processes and form metal-EDTA complexes [4–7,66–68]. Thus, in addition to metal ions reduction, the degradation of co-existing organic pollutants was also of vital importance. As illustrated in Fig. 8A and Fig. S10, the simultaneous PEC reduction of Cr(VI) and degradation of EDTA can be observed in the present system. Moreover, the reduction of Cr(VI) was greatly improved by the presence of EDTA. With an increasing EDTA concentration (Fig. 8B), the removal efficiency of Cr(VI) increased from 40% to 91% after 80 min of the PEC reaction. Meanwhile, the presence of other organics was also investigated. As shown in Fig. S11, the presence of either colorless phenol or colored MB dye can greatly promote the reduction of Cr(VI). The organics themselves were also degraded simultaneously. Thus, the Fe₂O₃-GQDs/NF-TiO₂ composite electrode was suitable for handling Cr(VI)-organic co-polluted wastewater.

Experiments with different initial solution pH were also performed, as pH has always been considered an important factor for Cr(VI) reduction. As shown in Fig. 9A, the reduction of Cr(VI) is easier to carry out under lower pH. The reason may be as follows: (1) The Cr(VI)/Cr(III) redox potential became larger at low pH due to the different predominant states of Cr(VI) ($E^0(\text{CrO}_4^{2-}/\text{Cr}(\text{OH})_3) = -0.13 \text{ V vs. NHE}$, $E^0(\text{HCrO}_4^-/\text{Cr}^{3+}) = 1.35 \text{ V vs. NHE}$) [69], which led to an increased thermodynamic driving force for Cr(VI) reduction; (2) The VB edge of the photoanode shifted along with the CB edge to a more positive position at lower pH, which led to increased oxidative ability for EDTA degradation [64] and subsequently more efficient electron-hole separation.

In the present study, the PEC experiments were performed using Na₂SO₄ as an electrolyte to increase conductivity. Thus, the concentration of Na₂SO₄ may also affect the PEC activity for Cr(VI) reduction [70]. As shown in Fig. 9B, the reduction of Cr(VI) was enhanced by increasing the Na₂SO₄ concentration. In addition, the enhancement trend slowed down when the Na₂SO₄ concentration was further increased to 1.0 M. In general, the above results indicate that the prepared photoanode is suitable for handling high-salinity wastewater.

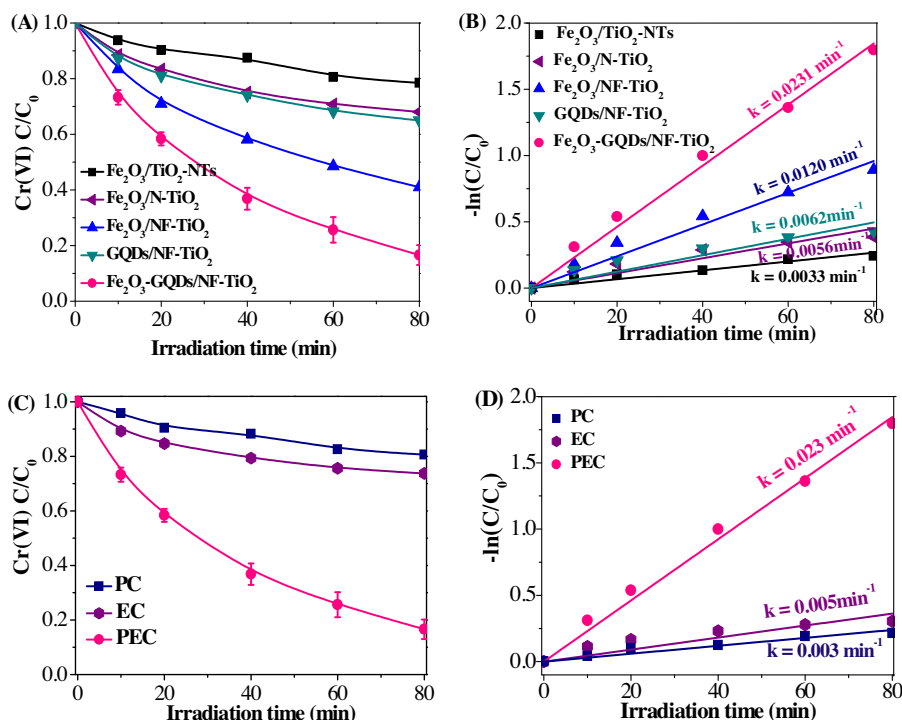


Fig. 6. (A) PEC reduction dynamics and (B) pseudo-first-order kinetic curves of Cr(VI) using different photoanodes; (C) Comparison of Cr(VI) reduction dynamics and (D) pseudo-first-order kinetic curves using Fe_2O_3 -GQDs/NF- TiO_2 electrode under different processes. Reaction conditions: 2.0 V, 0.2 M Na_2SO_4 , pH 3.0, 80 μM Cr(VI), 1 mM EDTA.

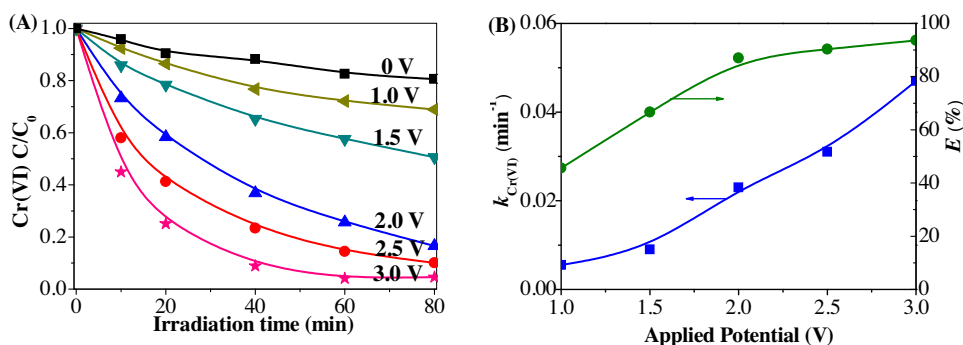


Fig. 7. Effect of external potential on the PEC reduction of Cr(VI) on Fe_2O_3 -GQDs/NF- TiO_2 under visible light irradiation (A) reduction dynamics, (B) estimated rate constants and $E\%$. Reaction conditions: 2.0 V, 0.2 M Na_2SO_4 , pH 3.0, 80 μM Cr(VI), 1 mM EDTA.

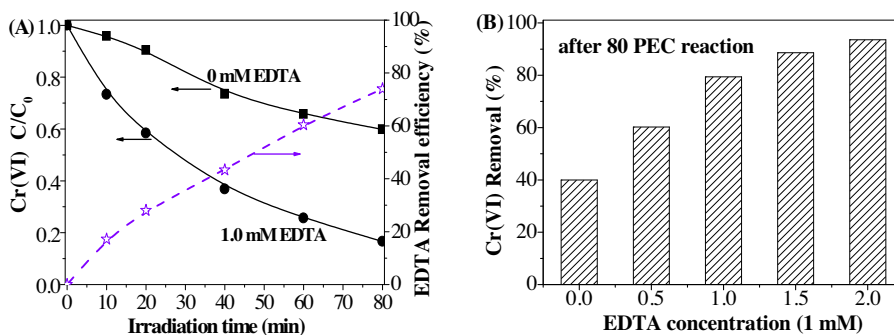


Fig. 8. (A) Effect of EDTA concentration on the PEC reduction of Cr(VI) (left) and simultaneous removal efficiency of 1.0 mM EDTA (right) using a Fe_2O_3 -GQDs/NF- TiO_2 electrode. (B) Relationship between Cr(VI) removal efficiency and coexisting EDTA concentration. External potential: 2.0 V. Electrolyte: 0.2 M Na_2SO_4 , pH = 3.0.

3.6. Stability of the Fe_2O_3 -GQDs/NF- TiO_2 electrode

As an excellent photocatalytic electrode, the stability of the PEC performance is critical. In the present study, the Fe_2O_3 -GQDs/NF-

TiO_2 film was evaluated via both a long-time photocurrent test and cyclic PEC experiments for Cr(VI) reduction. As shown in Fig. 10A, the photocurrent generated on the Fe_2O_3 -GQDs/NF- TiO_2

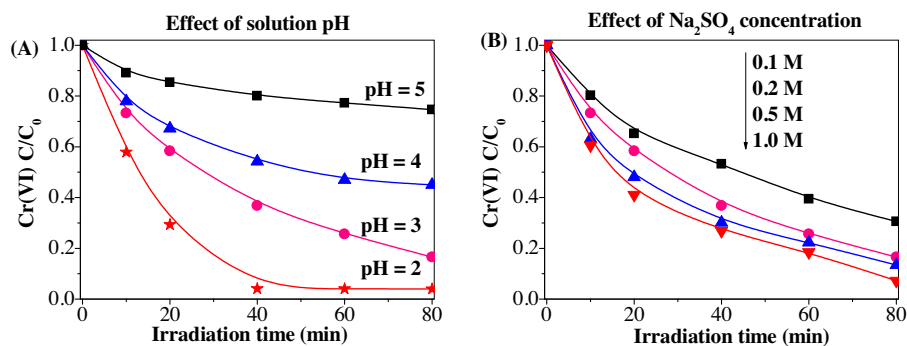


Fig. 9. (A) Influence of solution pH and (B) electrolyte concentration on the PEC reduction of Cr(VI). Reaction conditions: Fe₂O₃-GQDs/NF-TiO₂, 80 μ M Cr(VI), 1 mM EDTA.

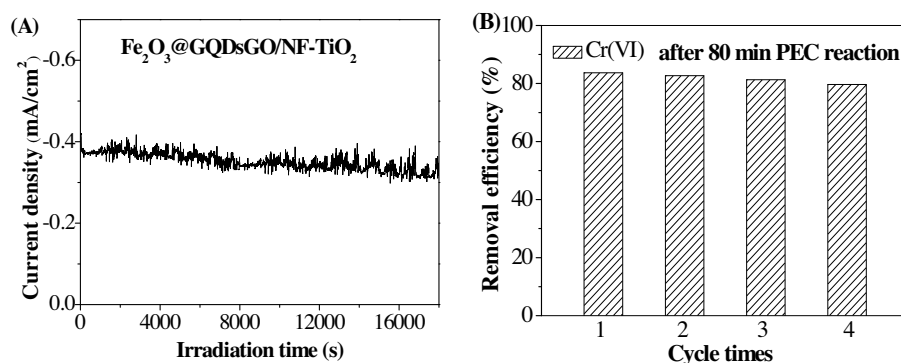


Fig. 10. (A) Long-time photocurrent decay curve measured under visible light irradiation at a constant potential of 0.5 V (vs. Ag/AgCl) for Fe₂O₃-GQDs/NF-TiO₂ film in 0.1 M Na₂SO₄ and Na₂SO₃ mixed aqueous solution; (B) Cyclic removal of both Cr(VI) and phenol using the Fe₂O₃-GQDs/NF-TiO₂ photoanode under visible light irradiation.

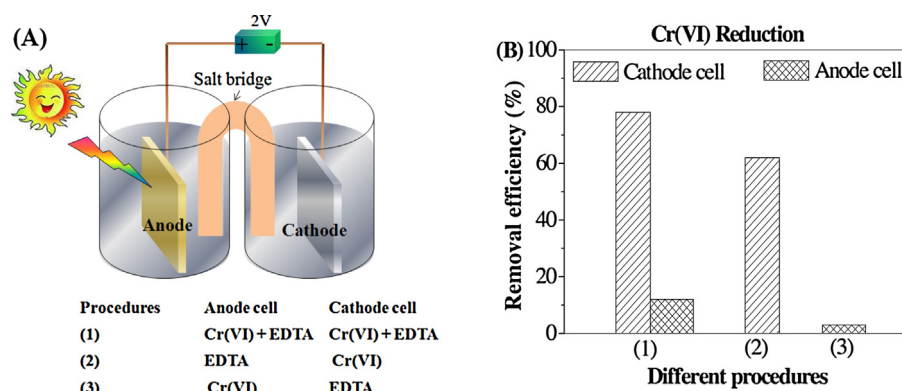


Fig. 11. (A) Schematic illustration of experiments using a salt bridge and (B) Cr(VI) removal efficiencies in different PEC processes. Reaction conditions: 2.0 V, 0.2 M Na₂SO₄, pH 3.0, 80 μ M Cr(VI), 1 mM EDTA.

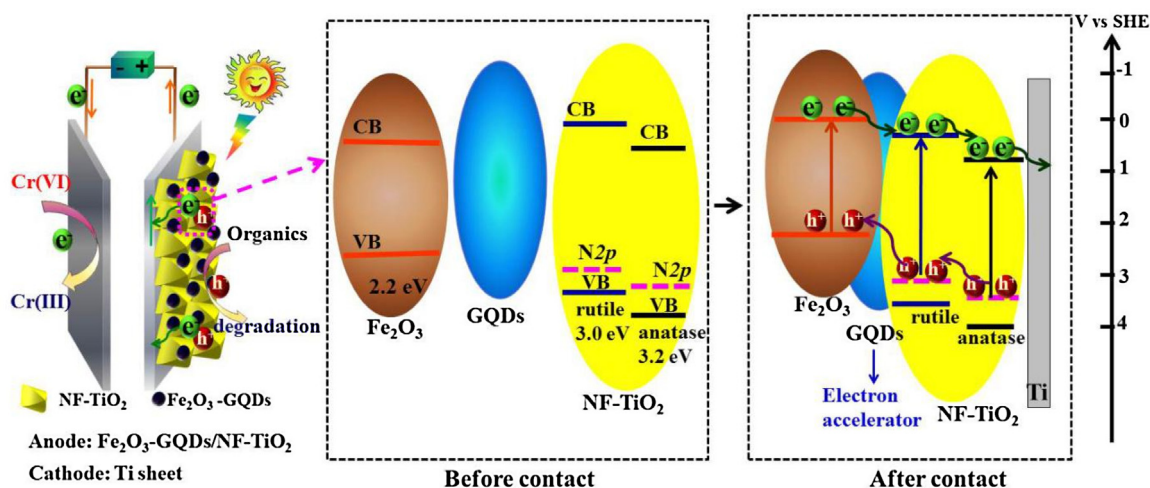
film was extremely stable and exhibited nearly no attenuation within 18,000 s (5 h) of constant visible light irradiation. The optimized film electrode was also tested in 4 successive cyclic PEC runs, and the results are presented in Fig. 10B. The removal efficiencies were relatively consistent over 4 cycles. Overall, the Fe₂O₃-GQDs/NF-TiO₂ film electrode exhibited superior PEC performance and stability.

3.7. Proposed mechanism

In the present study, the visible-light-active Fe₂O₃-GQDs/NF-TiO₂ film was applied as anode with a Ti sheet as cathode, respectively. The photogenerated electrons on the photoanode are anticipated to be driven to the cathode with the assistance of applied positive potential. In this manner, the photogenerated

holes left on the anode and electrons on the cathode will lead to subsequent oxidation and reduction reactions, respectively. Experiments using salt bridges were performed to verify this assumption (Fig. 11A). The PEC reduction of Cr(VI) was performed using two separate glass cells under different conditions, and the results are shown in Fig. 11B. It can be observed that Cr(VI) was predominately reduced in the cathode cell.

Based on all the above results and analyses, tentative mechanisms for the reduction of Cr(VI) and the separation/transfer of photogenerated electron-hole pairs on Fe₂O₃-GQDs/NF-TiO₂ are presented in Scheme 2. For NF-TiO₂, both anatase and rutile phases were identified by XRD analysis. Due to the different band gaps and CB positions [71–73], the intrinsic band difference between anatase and rutile TiO₂ will be beneficial for electron-hole separation. In addition, although α -Fe₂O₃ was reported to possess a lower inde-



Scheme 2. Schematic illustration for the PEC reduction of Cr(VI) (left) and the separation/transfer of photogenerated electron-hole pairs on Fe₂O₃-GQDs/NF-TiO₂ during the PEC process (right).

pendent CB position relative to TiO₂, the same Fermi level tended to be achieved between α -Fe₂O₃ and NF-TiO₂ when they were in contact with each other. In this manner, the CB of α -Fe₂O₃ would move to a more negative position [29]. XPS analysis (Fig. 3C) has shown that the introduction of GQDs will lead to the dispersion of electron density from the Fe atoms to the GQDs. Herein, the GQDs act as an electron accelerator, which will be beneficial for the process of electron transfer from Fe₂O₃ to TiO₂. Finally, the separated electrons will be driven to the cathode by an applied positive potential, and the holes will be kept on the photoanode. Thus, an efficient separation of photogenerated electron-hole pairs will be achieved due to the synergistic effect among Fe₂O₃, GQDs and NF-TiO₂.

4. Conclusion

In the present study, a visible-light active Fe₂O₃-GQDs/NF-TiO₂ composite film was fabricated by simultaneously loading α -Fe₂O₃ and GQDs onto pyramid-shaped NF-TiO₂. NH₄F plays a vital role in transforming tubular TiO₂-NTs into pyramid-shaped NF-TiO₂ with dominant (101) facets. Easier generation, separation and transfer of e^- - h^+ pairs was facilitated due to the combined effect of visible-light active components (α -Fe₂O₃ and NF-TiO₂) and excellent electron accelerators (GQDs). For example, electrochemical characterizations indicated that the visible-light-induced photocurrent density at 0.4 V vs. Ag/AgCl was approximately 4 times that on Fe₂O₃/TiO₂-NTs. Superior PEC activity for Cr(VI) reduction and stability were observed when using Fe₂O₃-GQDs/NF-TiO₂ as anode with a Ti sheet as cathode. The pseudo first-order rate constant $k_{Cr(VI)}$ increased by 7 times relative to that on Fe₂O₃/TiO₂-NTs. Furthermore, the selected photoanode also exhibited good stability in the long-time photocurrent test and reuse processes for Cr(VI) reduction. Overall, the present study developed a promising film electrode for environmental application, particularly for treating Cr(VI)-organic co-polluted wastewater.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.11.046>.

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